



TITLE:

A mathematical model for a hysteresis appearing in adsorption phenomena (New developments of the theory of evolution equations in the analysis of non-equilibria)

AUTHOR(S):

Aiki, Toyohiko; Murase, Yusuke; Sato, Naoki; Shirakawa, Ken

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CITATION:

Aiki, Toyohiko ...[et al]. A mathematical model for a hysteresis appearing in adsorption phenomena (New developments of the theory of evolution equations in the analysis of non-equilibria). 数理解析研究所講究録 2013, 1856: 1-11

ISSUE DATE:

2013-10

URL:

<http://hdl.handle.net/2433/195252>

RIGHT:

# A mathematical model for a hysteresis appearing in adsorption phenomena

日本女子大学・理学部 愛木豊彦 (Toyohiko Aiki)  
Department of Mathematical and Physical Sciences, Faculty of Science  
Japan Women's University

名城大学・理工学部 村瀬勇介 (Yusuke Murase)  
Department of Mathematics, Faculty of Science and Technology  
Meijo University

長岡工業高等専門学校・一般教育科 佐藤直紀 (Naoki Sato)  
Division of General Education  
Nagaoka National College of Technology

千葉大学・教育学部 白川健 (Ken Shirakawa)  
Department of Mathematics, Faculty of Education  
Chiba University

## 1 Introduction

In the present paper we propose an original mathematical model for a hysteresis appearing in adsorption phenomena. The mathematical model (FBP) will be given in Section 3 as a free boundary problem, in which the free boundary stands between the regions of moisture liquid and moisture vapor in one hole of a porous medium. The aim of this paper is to contribute researches for complex systems including hystereses through a discussion about a modeling process for the new mathematical description of the hysteresis.

Our study is motivated to overcome difficulties that arose in the works for three dimensional concrete carbonation process in [2, 3, 4]. In these papers a mathematical model for the process was proposed and studied taking into account of a hysteresis effect. The model consists of quasilinear diffusion equations with a hysteresis operator approximately described by a type of a play operator which is given by an ordinary differential equation including the subdifferential of the indicator function for a closed interval. Here, we note that the uniqueness question remains open in either of [2, 3, 4]. The difficulty of the uniqueness is caused by the fact that the continuous dependence between a solution and given data of quasilinear parabolic equations is not sufficient to conform to the continuous property of the play operator summarized as follows (see [12, 22] for details):

(\*) For a play operator  $\mathcal{P} : C([0, T]) \longrightarrow C([0, T])$  with  $0 < T < \infty$ ,

$$|\mathcal{P}(v_1) - \mathcal{P}(v_2)|_{C([0, T])} \leq C|v_1 - v_2|_{C([0, T])} \quad \text{for } v_1, v_2 \in C([0, T]),$$

where  $C$  is a positive constant.

When we consider the model for concrete carbonation, the input function  $v$  of the operator is a solution of the quasilinear parabolic equation and the output function  $w = \mathcal{P}(v)$  appears in the coefficient of the equation. In most of quasilinear parabolic equations, it is not easy to obtain an estimate for difference of solutions with respect to a topology of the space of continuous functions. Thus it is not easy to prove the uniqueness.

In order to overcome these difficulties we can choose the following two ways. The first way is to improve continuous properties of solutions to the quasilinear parabolic equation. The second one is to develop a new mathematical description of a hysteresis operator. For the past years the mathematical treatment with the ordinary differential equations was applied for the study to various mathematical models for nonlinear phenomena. Also, the following advantages of such a treatment were pointed out in [1]. One of advantages is to approximate them easily and the other is to enable to describe change of the hysteresis by perturbation of given data. However, as mentioned above this treatment has a weakness on the continuous property. Moreover, for the treatment it is hard to express a behavior inside of the hysteresis loop, because the treatment is just a phenomenologically approach. Then, based on these arguments we choose the second way as a strategy in this paper, and hence our main aim is to propose a new model for a hysteresis appearing in adsorption process by consideration for a mechanism, in detail.

The discussion of this paper will be proceeded as follows. In the next Section 2, we briefly see the hysteresis operators appearing in adsorption phenomena. Due to this observation our original model (FBP) is stated in Section 3. In Section 4 we consider an algorithm to obtain approximate solution, and show some data of numerical experiments associated with (FBP). Finally, in Section 5, we comment about the adequacy of (FBP) by taking into account the numerical data, and discuss about the future prospects.

## 2 Adsorption phenomenon

In this section we focus the relationship between the humidity and the saturation describing an adsorption phenomenon (see [16]). The hysteresis is a type of input-output relationship between the humidity and the saturation in one hole of a porous medium. From the experimental data (Figure 1) we have the following three features on the behavior of the graph:

- Around ① and ③ the slopes are steep.
- Around ② the slope is gradual.
- The loop depends on the historical data.

The scenario for the behavior the relationship is described as follows (see Figure 2 to get general schemes of the ideas): We consider one hole of the porous medium and suppose that the degree of saturation can be regarded as the volume ratio of the liquid in the hole. When the humidity is low, moisture vapor touches the wall directly and becomes moisture liquid. After the surface of the wall is covered with moisture liquid, moisture vapor touches the liquid and becomes liquid. Since attractive force between the wall and the vapor is much stronger than the force between vapor and liquid, the

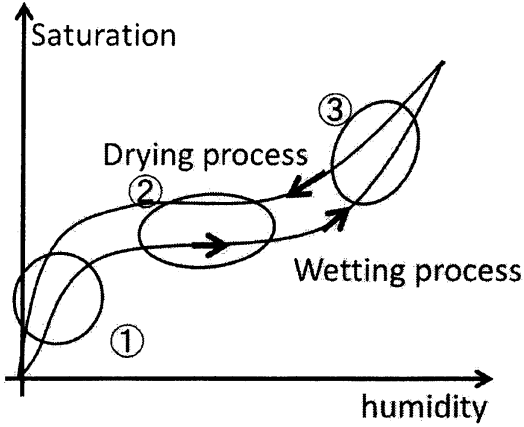


Figure 1: Adsorption

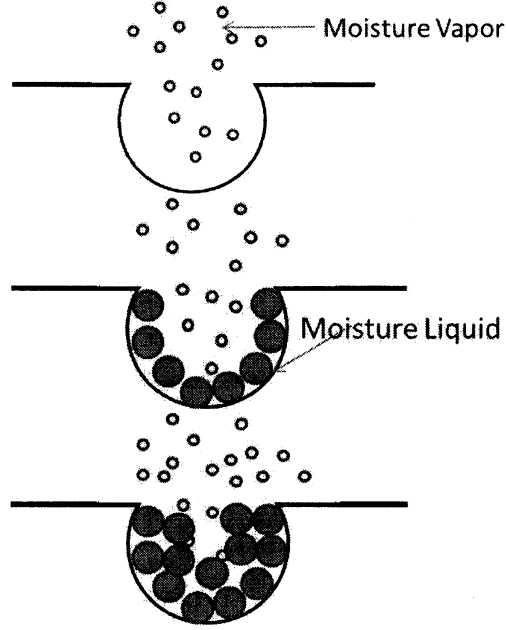


Figure 2: Scenario of adsorption

slope will be gradual as the humidity becomes high. When the humidity rises further, the slope becomes steeper, since the probability that the vapor touches the liquid in the hole is also high.

Therefore, the aims of this research are to propose a mathematical model representing the above scenario and to confirm that the above graph obtained from numerical simulations for the model.

### 3 Mathematical modeling for adsorption

In this section we shall propose our mathematical model for adsorption phenomena. First, we simplify a hole in the porous medium as one dimensional compact interval  $[0, L]$ , where  $L$  indicates the depth of the hole. Moreover, we assume that at  $x = 0$  the wall exists, from the point  $x = L$  the atmosphere flows into the hole, and the domain  $[0, L]$  is separated by the liquid region  $(0, s)$  and the vapor region  $(s, L)$  (see Figure 3). Under these assumptions we define the degree of saturation  $w$  by

$$w = \frac{s}{L}.$$

In this paper the humidity  $u = u(t, x)$  indicates the ratio of volume of moisture vapor per unit volume for any time  $t$  and the spatial position  $x$ . Then the mass conservation leads to

$$\rho_v u_t + j_x = 0 \quad \text{in } (s, L),$$

where  $\rho_v$  is the density of moisture vapor and  $j$  is the diffusion flow of vapor. Fick's law

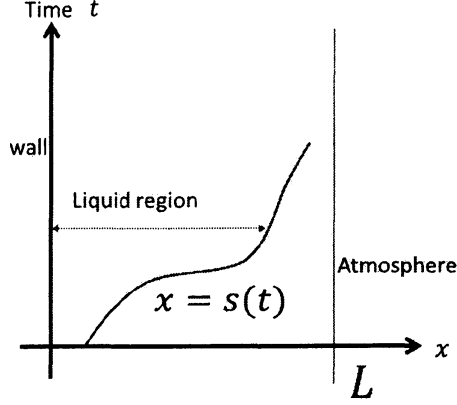


Figure 3: One-dimensional model

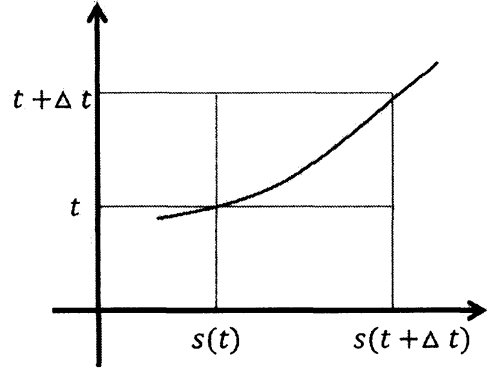


Figure 4: Near the free boundary

implies that  $j = -\kappa u_x$  and

$$\rho_v u_t - \kappa u_{xx} = 0 \quad \text{in } (s, L),$$

where  $\kappa$  is a diffusivity constant.

Next, we consider the mass conservation of moisture near the free boundary  $x = s(t)$  for  $t > 0$ . If  $s'(t) > 0$ , then for small  $\Delta t > 0$  the mass of vapor of the interval  $(s(t), s(t + \Delta t))$  is given by

$$\int_{s(t)}^{s(t+\Delta t)} \rho_v u(t, x) dx.$$

Also, the mass of liquid on  $(s(t), s(t + \Delta t))$  at time  $t + \Delta t$  is given by

$$\rho_w (s(t + \Delta t) - s(t)),$$

where  $\rho_w$  is the density of moisture liquid (see Figure 4). Then, it holds that

$$\rho_w (s(t + \Delta t) - s(t)) = \int_{s(t)}^{s(t+\Delta t)} \rho_v u(t, x) dx - \Delta t \times j(t, s(t + \Delta t)),$$

and by letting  $\Delta t \rightarrow 0$  we have

$$\rho_w s'(t) = \rho_v s'(t) u(t, s(t)) + \kappa u_x(t, s(t)).$$

We note that the above equation also holds in case  $s'(t) \leq 0$ .

According to the scenario shown in the previous section the dynamics of the free boundary depends on the distance between the wall and the front of the liquid region, and the humidity at the front. Then we assume

$$s'(t) (= \frac{d}{dt} s(t)) = \alpha(s(t), u(t, s(t))) \quad \text{for } t > 0, \quad (3.1)$$

where  $\alpha : \mathbf{R}^2 \rightarrow \mathbf{R}$  is continuous.

Here, from simple observations we can give some assumptions for  $\alpha$ . First, as the humidity at the front is high, the vapor can easily become moisture liquid. This implies

$$\frac{\partial}{\partial u}\alpha(s, u) > 0 \quad \text{for } (s, u) \in \mathbf{R}^2. \quad (3.2)$$

Next, if the humidity is extremely high, then the front must grow. Also, if the humidity vanishes, then the front can not grow. Namely, for any  $s \in \mathbf{R}$  it should be that

$$\alpha(s, u) \geq 0 \text{ for } u \geq 1 \text{ and } \alpha(s, u) \leq 0 \text{ for } u \leq 0. \quad (3.3)$$

Moreover, since the front of liquid region can not grow beyond the gate of the hole and the wall, we can suppose that for any  $u \in \mathbf{R}$

$$\alpha(s, u) \leq 0 \text{ for } s \geq L \text{ and } \alpha(s, u) \geq 0 \text{ for } s \leq 0. \quad (3.4)$$

Thus we have obtained the following free boundary problem (FBP) to find a pair  $\{s, u\}$  of a curve  $x = s(t)$  on  $[0, T]$ ,  $0 < T < \infty$ , and a function  $u = u(t, x)$  on  $Q_s(T) := \{(t, x) | s(t) < x < L, 0 < t < T\}$  satisfying

$$\rho_v u_t - \kappa u_{xx} = 0 \quad \text{in } Q_s(T), \quad (3.5)$$

$$u(t, L) = g(t) \quad \text{for } 0 < t < T, \quad (3.6)$$

$$u(0, x) = u_0(x) \quad \text{for } s_0 < x < L,$$

$$s'(t) = \alpha(s(t), u(t, s(t))) \quad \text{for } 0 < t < T,$$

$$\kappa u_x(t, s(t)) = (\rho_w - \rho_v u(t, s(t)))\alpha(s(t), u(t, s(t))) \quad \text{for } 0 < t < T, \quad (3.7)$$

$$s(0) = s_0,$$

where  $s_0$  is a initial position of the free boundary, and  $g$  and  $u_0$  are given boundary and initial functions on  $[0, T]$  and  $[s_0, L]$ , respectively. In [20] we establish the well-posedness for the above problem under the assumptions (3.2)  $\sim$  (3.4).

## 4 Numerical simulation

In this section we consider the problem (FBP) and present its numerical simulation. First, we show the values of constants in (FBP) as the following Table 1:

$L$	$\kappa$	$\rho_w$	$\rho_v$	$s_0$
1	1	1	$1.73 \times 10^{-5}$	0.01

Table 1: Values of constants

Also, we set  $u_0(x) = 0$  for  $x \in (s_0, L)$ .

Here, we give two remarks concerned with a numerical simulation to (FBP) as follows:

1. (FBP) is a free boundary problem so that the domain  $(s(t), L)$  is unknown for each time  $t$ , where  $\{s, u\}$  is a solution of (FBP). Moreover, since the value of  $u(t, s(t))$  is also unknown, it is not easy to extend  $u$  on the fixed interval, for example  $[0, L]$ , smoothly as a usual one-phase Stefan problem.

2. There is a big difference between orders of  $\rho_v$  and  $\rho_w$ . By this it takes a lot time to calculate the solution, numerically. We see this property if the original domain maps into cylindrical domain by change of variable, especially.

Hence, in order to solve these problems we develop the following algorithm for our numerical simulations. For  $\Delta t > 0$  we find approximations of  $s(n\Delta t)$  and  $u(n\Delta t, x)$  for  $n = 1, 2, \dots$ , and  $x \in (s(n\Delta t), L)$ . As you see the algorithm, the number of lattice points and the mesh size on space depend on  $n$  so that we denote them by  $N_n$  and  $(\Delta x)_n$  for each  $n$ . Thus we calculate  $s_n$  and  $u_n^{(i)}$  as approximations of  $s(n\Delta t)$  and  $u(n\Delta t, s(n\Delta t) + i(\Delta x)_n)$ , respectively, for  $n$  and  $i = 0, 1, \dots, N_n$ .

**Step 1.** Set  $n = 0$ ,  $s_n = s_0$ ,  $N_n = 40$ , and  $u_n^{(i)} = u_n(s_n + i(\frac{L - s_n}{N_n}))$  for  $i = 0, 1, \dots, N_n$ .

**Step 2.** Set  $(\Delta x)_n = \frac{L - s_n}{N_n}$ .

**Step 3.** Set  $u_n^{(-1)} = u_n^{(1)} - \frac{2(\Delta x)_n}{\kappa}(\rho_w - \rho_v u_n^{(0)}) \times \alpha(s_n, u_n^{(0)})$ .

**Step 4.** Put  $s_{n+1} = s_n + \Delta t \times \alpha(s_n, u_n^{(0)})$ .

**Step 5.** Let  $N'_{n+1} = \max\{j \in \mathbf{N} | j \leq \frac{L - s_{n+1}}{0.025}\}$ ,  $N_{n+1} = \max\{\min\{40, N'_{n+1}\}, 10\}$  and  $(\Delta x)_{n+1} = \frac{L - s_{n+1}}{N_{n+1}}$ .

**Step 6.** Compute  $\bar{u}^{(i)}$  from  $u_n^{(i)}$  for  $i = -1, 0, 1, \dots, N_{n+1}$  by using the Lagrange interpolation with degree  $1 + N_{n+1}$ , where  $\bar{u}^{(i)}$  is corresponding to an approximation of  $u(n\Delta t, L - i(\Delta x)_{n+1})$ .

**Step 7.** Compute  $u_{n+1}^{(i)}$  for  $i = 0, 1, \dots, N_{n+1}$  as an approximate solution satisfying (3.5), (3.6) and (3.7) from  $\bar{u}_n^{(i)}$  by using the Gauss-Seidel method.

**Step 8.** Set  $n := n + 1$  and GO TO Step 2.

In order to verify the correctness of our algorithm we put

$$s(t) = \frac{3}{4}(1 - e^{-t}) + \frac{1}{4}, \quad u(t, x) = (1 + \sin \pi x)e^t,$$

$$\alpha(s, u) = (1 + u^2) \left( u - \frac{\arctan(10s - 6) - \arctan(-6)}{\arctan(4) - \arctan(-6)} \right).$$

Then,  $u$  and  $s$  satisfy

$$\begin{aligned} \rho_v u_t - \kappa u_{xx} &= f \quad \text{in } Q_s(T), \\ u(t, L) &= g(t) \quad \text{for } 0 < t < T, \\ u(0, x) &= u_0(x) := 1 + \sin \pi x \quad \text{for } s_0 < x < L, \\ s'(t) &= \alpha(s(t), u(t, s(t))) + k(t) \quad \text{for } 0 < t < T, \\ \kappa u_x(t, s(t)) &= (\rho_w - \rho_v u(t, s(t))) (\alpha(s(t), u(t, s(t))) + k(t)) + h(t) \quad \text{for } 0 < t < T, \\ s(0) &= s_0 := \frac{1}{4}, \end{aligned}$$

where  $f(t, x) = (\rho_v + (\rho_v + \kappa\pi^2) \sin \pi x)e^t$ ,  $g(t) = e^t$ ,  $k(t) = \frac{3}{4}e^{-t} - \alpha(s(t), u(t, s(t)))$  and  $h(t) = \kappa\pi e^t \cos(\pi s(t)) - \frac{3}{4}(\rho_w - \rho_v u(t, s(t)))e^{-t}$  for  $(t, x) \in Q_s(T)$  for  $T > 0$ .

Since we know the exact solution of the above problem, we can calculate errors of approximate solutions obtained by our algorithm and summarize these errors as the following Table 2:

$\Delta t$	$10^{-3}$	$10^{-4}$	$10^{-5}$
	0.000372411	0.0000372467	0.00000372473

Table 2: Errors

From these results we infer that our method is somehow effective to (FBP). Then by using this algorithm we obtain the following solutions.

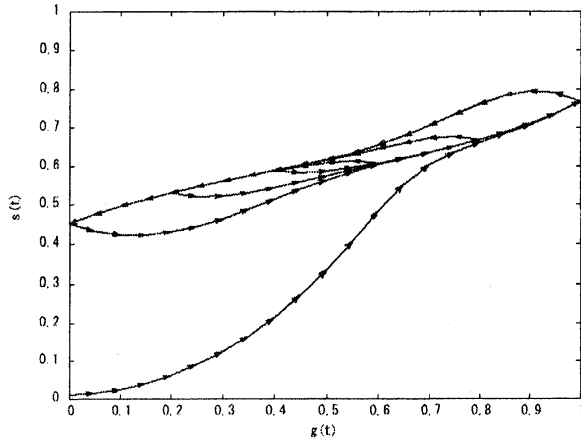


Figure 5: Simulation 1

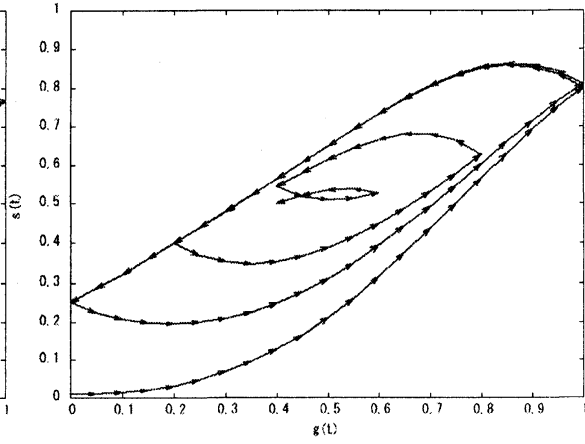


Figure 6: Simulation 2

In Simulation 1 (Figures 5) we set

$$\alpha(s, u) = (1 + u^2) \left( u - \frac{\arctan(10s - 6) - \arctan(-6)}{\arctan(4) - \arctan(-6)} \right),$$

and

$$g(t) = \begin{cases} \frac{t}{5} & (0 < t \leq 5), \\ 2 - \frac{t}{5} & (5 < t \leq 10), \\ \frac{t}{5} - 2 & (10 < t \leq 15), \\ 4 - \frac{t}{5} & (15 < t \leq 19), \\ \frac{t}{5} - 3.6 & (19 < t \leq 22), \\ 5.2 - \frac{t}{5} & (22 < t \leq 24), \\ \frac{t}{5} - 4.4 & (24 < t \leq 25), \\ 5.6 - \frac{t}{5} & (25 < t \leq 26). \end{cases} \quad (4.1)$$

Also, in Simulation 2 (Figures 6) we set

$$\alpha(s, u) = (1 + u^2)(\beta(u) - \gamma(s)),$$



where

$$\beta(u) = \begin{cases} 0 & \text{if } u < 0, \\ \frac{1-\cos(\pi u)}{2} & \text{if } u \in [0, 1], \\ 1 & \text{if } u > 1, \end{cases} \quad \gamma(s) = \begin{cases} 0 & \text{if } s < 0, \\ \frac{1-\cos(\pi s)}{2} & \text{if } s \in [0, 1], \\ 1 & \text{if } s > 1, \end{cases}$$

$g$  is given by (4.1).

From observations these graphs in Figures 5 and 6 we can conclude that:

- Since most of the ascending branches are located under descending ones, our graphs are quite similar to graphs obtained by experiments. In this sense we can represent the hysteresis in the absorption phenomena by (FBP).
- Our graphs do not have the features mentioned in Section 2. More precisely, the slopes for the low and high humidities are gradual in Figure 5 and the slope for the low humidity is too, in Figure 6. Hence, we need to find a better form of  $\alpha$  to reproduce the scenario as in Figure 1.

## 5 Conclusion and discussion

In this section we discuss about (FBP) in terms of numerical simulation, mathematical analysis and application to concrete carbonation process.

### 5.1 Numerical simulation

As mentioned in Section 4, by using (FBP) we can obtain appropriate graphs to describe the hysteresis in adsorption phenomena, and more accurate approximation to experiment data still remains as a significant challenge.

Additionally, we do not prove yet, whether our algorithm outputs certain approximate solutions of (FBP), or not. This is also our future problem.

### 5.2 Mathematical analysis

Here, we show the challenge in the mathematical analysis of (FBP), referring to similar free boundary problem. The reference problem was proposed as a mathematical model for concrete carbonation and discussed by Böhm and Muntean in [17, 19]. Recently, the simplified model of the problem was studied. The problem (CC) is to find a curve  $x = \ell(t)$  for  $0 < t < T$ ,  $T > 0$ , and functions  $w$  and  $v$  on  $Q_\ell(T) = \{(t, x) | 0 < x < \ell(t), 0 < t < T\}$

satisfying

$$\begin{aligned}
w_t - (\kappa_1 w_x)_x &= f(w, v) \quad \text{in } Q_\ell(T), \\
v_t - (\kappa_2 v_x)_x &= -f(w, v) \quad \text{in } Q_\ell(T), \\
w(t, 0) &= h_1(t), v(t, 0) = h_2(t) \quad \text{for } 0 < t < T, \\
w(0, x) &= w_0(x), v(0, x) = v_0(x) \quad \text{for } 0 < x < \ell_0, \\
\ell'(t) &= \frac{d}{dt} \ell(t) = \psi(w(t, \ell(t))) \quad \text{for } 0 < t < T, \\
\kappa_1 w_x(t, \ell(t)) &= -\psi(w(t, \ell(t))) - \ell'(t)w(t, \ell(t)) \quad \text{for } 0 < t < T, \\
\kappa_2 v_x(t, \ell(t)) &= -\ell'(t)v(t, \ell(t)) \quad \text{for } 0 < t < T, \\
\ell(0) &= \ell_0,
\end{aligned}$$

where  $\kappa_1$  and  $\kappa_2$  are positive constants,  $f$  is a given continuous function on  $\mathbb{R}^2$ ,  $h_1$  and  $h_2$  are boundary data,  $w_0$ ,  $v_0$  and  $\ell_0$  are initial data and  $\psi(r) = \kappa_0 |[r]^+|^p$  where  $\kappa_0 > 0$  and  $p \geq 1$  are given constants. In this problem  $w$  and  $v$  represent the mass concentration of carbon dioxide dissolved in water and in air, respectively, while  $\ell(t)$  denotes the position of the penetration reaction front in concrete at time  $t > 0$ . The interface  $\ell$  separates the carbonated from the non-carbonated regions.

For this problem the existence, the uniqueness of a weak solution and the large time behavior of the free boundary were investigated in [5, 6, 7, 8, 9, 10, 11]. As compared to the concrete carbonation model (CC), our problem (FBP) has the following features. The first one is that the time derivative of the free boundary depends on the position of the free boundary (see (3.1)). Secondly, in (FBP) we cannot know the sign of the derivative of the free boundary a priori, while in (CC) we can show that it is always nonnegative. On the other hand, we can not know the sign of the derivative of the free boundary a priori for (FBP). Due to these facts, it becomes not easy to obtain the global estimate for the derivative of the free boundary. This leads to the difficulty to show the convergence of the free boundary  $s(t)$  of (FBP) as  $t \rightarrow \infty$ , although it looks a natural event in physics. Therefore, up to a research to a large time behavior of the free boundary we possibly need to improve our model.

### 5.3 Application to concrete carbonation

Finally, we show much further challenge of this study. Indeed, we have a future prospect to consider a coupled system which consists of the quasilinear parabolic equation associated with the concrete carbonation, and the free boundary problem (FBP) in the adsorption.

In previous works relationship between the the humidity and the degree of saturation is described by an operator so that we can make a mathematical model only to combine the differential equation and the operator. However, when we propose a system containing (FBP) which is a model for concrete carbonation, it is necessary to show a certain physical interpretation. To this end, we will adopt a two-scale modeling as this interpretation.

The two-scale problem was already studied in [15]. Recently, this idea was used in the analysis for reaction diffusion system (see [18, 21, 13, 14]). By using the idea of the

two-scale modeling we can deal with macro and micro domains, and macro and micro parameters at the same system. Accordingly, after we clarify the continuous dependence between the humidity  $g$  and the degree of saturation  $s$  on (FBP), and the large time behavior of the free boundary, we will propose and study the couple combined by the two-scale modeling.

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